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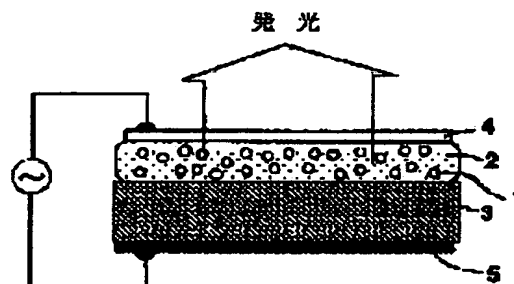
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## (54) ELECTROLUMINESCENT ELEMENT AND ITS MANUFACTURE

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an EL element having highly efficient luminescence with a simple treatment process, by utilizing a dielectric insulating layer having translucency and a high dielectric constant at a low temperature formed by using high quality and high crystalline property retained by sulfuric phosphor powder and oxidic phosphor powder used in the past has, and a Sol-gel method.

**SOLUTION:** In this manufacturing method, a deposited luminescent layer comprising translucent dielectric layer 2 with a high dielectric constant to be dispersed with at least one kind of phosphor powder 1 is formed on an electrode layer having a metal membrane or a transparent conductive membrane formed on a ferroelectric ceramic sheet such as barium titanate, glass or ceramic serving as a base 3, and an EL element having a structure having the deposited layer sandwiched by a transparent layer 4 and a confronting electrode layer 5 is provided. The deposited layer contains the phosphor powder 1 dispersed, partially dispersed and partially deposited or entirely deposited and comprises a translucent dielectric layer with a high dielectric constant.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The electroluminescent element to which at least one sort of fluorescent substance powder is characterized by the structure which formed on the base distribution or the deposition luminous layer which consists of deposition or a translucency quantity dielectric constant inorganic dielectric layer all deposited on the base on a distributed part base, and was inserted in the transparent electrode layer and the counterelectrode layer in part.

[Claim 2] The electroluminescent element according to claim 1 said whose base is a ferroelectric ceramic sheet.

[Claim 3] The electroluminescent element according to claim 1 characterized by forming a deposition luminous layer according to claim 1 on the metal thin film formed on the base which is glass or a ceramic, or a transparent conductive thin film electrode layer, and coming to form a transparent conductive electrode layer or a metal-electrode layer on it.

[Claim 4] The manufacturing method of the electroluminescent element according to claim 1, 2, or 3 using the deposition luminous layer which performs and forms baking or heat treatment in a controlled atmosphere under the conditions of the range which leaves the translucency of this dielectric layer after using a sol-gel method and forming on a base the translucency quantity dielectric constant inorganic dielectric layer which constitutes a deposition luminous layer according to claim 1.

[Claim 5] The manufacturing method of the electroluminescent element according to claim 4 which puts in order and forms each deposition luminous layer which consists of two or more sorts, for example, red, and three sorts of fluorescent substances which are green and blue and emit light using a patterning technique on the same field using a manufacturing method according to claim 4.

[Claim 6] The manufacturing method of the electroluminescent element according to claim 4 or 5 used for manufacturing an illumination lamp and a display.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to an electroluminescent element and its manufacturing method.

[0002]

[Description of the Prior Art] An electroluminescent element (it is called an EL element below) is studied to the application to a plan type solid-state luminescence display for many years, and has deep-rooted expectation to the utilization. This EL element On structure, A metal thin film or a transparent conductive thin film The piece discontinuous construction or this fluorescent substance luminous layer thin film which consists of a crystalline fluorescent substance luminous layer thin film and a crystalline dielectric insulating-layer thin film on the thin film which consists of duplex discontinuous construction inserted with this dielectric insulating-layer thin film on the formed glass or a plastic film substrate a transparent electrode layer or a metal thin film electrode layer It is divided into the organic distributed type characterized by inserting the luminous layer which makes homogeneity come to carry out distributed binding of the thin film form characterized by forming, and the fluorescent substance powder into an organic system dielectric binder in a transparent electrode layer and a counterelectrode layer. Conventionally, about the luminescent color of an EL element, only the thing of green luminescence and bluish green color luminescence in Cu addition zinc sulfide (ZnS:Cu) system organic distributed alternating current drive thin film EL element is used for the yellow orange luminescence list in Mn addition zinc sulfide (ZnS:Mn) system or a terbium addition zinc sulfide (ZnS:Tb) system duplex discontinuous construction alternating current drive thin film EL element.

[0003]

[Problem(s) to be Solved by the Invention] In the case of the above-mentioned thin film form EL element, the electric field which a fluorescent substance luminous layer and a dielectric insulating layer are inserted in a serial to an external power, and require them for this luminous layer by any type of a piece insulation and duplex discontinuous construction become remarkably weak, and high brightness luminescence is not obtained. Therefore, it has translucency and development of the dielectric insulating layer of a high dielectric constant has been a technical problem. On the other hand, the crystallinity of this thin film luminous layer is raised, and when elevated-temperature heat treatment for obtaining high brightness luminescence more uses the glass substrate, there is a problem that it cannot introduce. Then, it is pressing need to realize the thin film luminous layer which was excellent in crystallinity with low temperature. On the other hand, although the thin film EL element which introduced the high dielectric constant ceramic sheet as this insulating layer is proposed, since the processing conditions for making it function as this insulating layer and the processing conditions of this fluorescent substance luminous layer do not have consistency, there is a trouble that a treatment process will become complicated. In addition, in a fluorescent substance thin film, especially the latest plural system oxide fluorescent substance thin film, even if it can perform elevated-temperature heat treatment, since it is difficult, raising the crystallinity will have the problem that high luminous efficiency like fluorescent substance powder is unrealizable. In the case of the distributed EL element, compared with the thin film EL element, the component structure was very easy, but the binder used conventionally had the problem that a dielectric constant could not impress high electric field to a fluorescent substance efficiently low therefore. The fluorescent substance which can be used practical is only principle top Cu addition zinc sulfide, the component which has high luminescence brightness was not obtained, but the luminescent color was also restricted. And since sulfide

system fluorescent substance ingredients, such as zinc sulfide, were sensitive to moisture, when making a component drive for a long time, they had to take the severe measures against moisture proof, and had become the greatest factor of a raise in cost.

[0004]

[Means for Solving the Problem] Recently, researches and developments of the high brightness EL element which used the very strong oxide system fluorescent substance for the luminous layer to moisture are activating. for example, the sintering barium titanate ( $\text{BaTiO}_3$ ) ceramic top which is a ferroelectric as Japanese Patent Application No. 2-254649 which becomes applicants' invention and Japanese Patent Application No. 2-256474, and a substrate-cum-an insulating layer -- Mn addition silicic acid of a silicate system fluorescent substance -- zinc ( $\text{Zn}_2\text{SiO}_4\text{:Mn}$ ) -- the EL element in which the thin film luminous layer was formed is realized. very -- recently -- Mn addition zinc gallate ( $\text{Zn}_2\text{GaO}_4\text{:Mn}$ ) [-- : in a patent application -- high brightness green luminescence is realized in the thin film EL element using Japanese-Patent-Application-No. 7-212332]. further -- Mn addition oxidation gallium-calcium-oxide [-- : in a patent application -- high brightness luminescence is realized in the thin film EL element using Japanese-Patent-Application-No. 9-95131].

[0005] In order that this invention may carry out one effort solution of the above-mentioned technical problem, the dielectric insulating layer which has translucency and a high dielectric constant at the low temperature formed with the high crystallinity sulfide system fluorescent substance powder used from the former, high crystallinity oxide system fluorescent substance powder which was described above, and a sol-gel method tends to be used, and it is going to realize the EL element which has efficient multicolor luminescence by the easy treatment process. Namely, on the electrode layer which formed a metal thin film or transparent conductive thin film:4 in this invention on the glass shown as a base 6 of ferroelectric ceramic sheet:3, such as barium titanate of drawing 1 and drawing 2, or drawing 3, or a ceramic as shown in drawing 1 - drawing 3 As at least one sort of fluorescent substance powder shows 1 of drawing 1, distribution or the deposition luminous layer which consists of distributed part deposition or translucency quantity dielectric constant inorganic dielectric layer:2 all deposited in part as shown in 1 of drawing 2 is formed. This EL element that has the structure inserted in the transparent electrode layer 4 and the counterelectrode layer 5 is offered. It is important to consist of the high dielectric constant inorganic dielectric layer in which this deposition luminous layer has translucency, including fluorescent substance powder here. Applicants have invented conventionally the EL element of the structure which sandwiched the luminous layer which consists of deposits which serve as a powder fluorescent substance made to deposit on a base from this powder fluorescent substance, congener, or a different-species thin film fluorescent substance on it with the transparent electrode and the counterelectrode [patent application Naka:Japanese Patent Application No. 8-95958]. In such an EL element, it is necessary to impress high electric field to homogeneity for the powder fluorescent substance deposited on the base, and a big electrical potential difference must be applied to this component. Therefore, the technique of impressing homogeneity quantity electric field to this powder fluorescent substance layer is taken by introducing an insulating layer, and impressing a very big electrical potential difference from the outside, or adopting a high dielectric constant dielectric ceramic sheet (opaque) as this insulating layer. By having introduced the transparent high dielectric constant inorganic dielectric layer which was not able to be conventionally realized instead of a thin film fluorescent substance layer (a transparent fluorescent substance deposit is included) which was described above, as a base, it is the point which can also use glass and a ceramic and is enabling broad application, and differs [ greatly ] from the configuration of the conventional thin film EL element and is epoch-making not to mention a ferroelectric ceramic in the EL element which becomes this invention on the other hand. By the way, this deposition luminous layer that constitutes the EL element which becomes this invention The metal salt, organometallic complex containing this fluorescent substance powder and each configuration element of this dielectric layer, Start ingredients, such as an alkoxide, acetate, or acetylacetonate, are used. a sol -- producing -- for example, the inside of this sol -- fluorescent substance powder -- mixed distribution or a part, distributed part deposition or after making all deposit Or after mixing each sol containing each configuration element, hydrolysis and desiccation gel are formed for this sol, and the purpose of this invention is attained by heat-treating in the range which left translucency succeedingly.

[0006] In addition, an ingredient with the above-mentioned well-known transparent electrode layer, for example, a tin oxide system, an indium oxide system, That it can form by a usual vacuum deposition method or a usual spatter etc. using the multiple oxide system transparence electric conduction film

ingredient containing a zinc-oxide system or II group, an III group, or at least one IV group element, of course it can also form using said same process using the organic solution containing the metal salt containing at least one sort of II groups, an III group, or IV group element, an organometallic complex, an alkoxide, acetate, or acetylacetonate.

[0007] On the other hand, in this invention, after forming the above-mentioned deposition luminous layer, it has proposed that this EL element can be manufactured by performing baking or heat treatment in the range which left translucency into the oxidizing atmosphere which controlled the inside of a controlled atmosphere, i.e., nitrogen gas, or air, or oxygen tension.

[0008]

[Function] In the EL element concerning this invention, it has the structure where the high quality quantity crystallinity which fluorescent substance powder (it is generally baking powder.) has is utilizable for the maximum. Moreover, adoption of spherical fluorescent substance powder is effective in raising a filling factor. Furthermore, since crystallinity is excellent, when the generation effectiveness of the hot electron at the time of high electric-field impression increases, fluorescent substance powder of excitation efficiency of an emission center improves sharply, and has the operation effectiveness that high luminescence brightness is obtained. Furthermore, the EL element which becomes this invention can be manufactured practical very cheaply from it being simple component structure. Moreover, this component structure that becomes this invention has the degree of freedom which can offer the EL element of double discontinuous construction called a metal-insulator-semi-conductor-insulator, when this fluorescent substance powder offers the EL element of piece discontinuous construction called a metal-insulator-semi-conductor or double discontinuous construction called a metal-insulator-semi-conductor-insulator in part distributed part deposition or when having deposited all, and it is distributing on a base. Since this dielectric layer has translucency and it has the large dielectric constant with any structure in addition to the ability to use the light from this fluorescent substance effectively, there is the operation effectiveness that high electric field can be impressed effective in this fluorescent substance. Furthermore, in the EL element which becomes this invention, since this fluorescent substance is surrounded in the translucency quantity dielectric constant inorganic dielectric layer, it is not necessary to take installation and the cure against moisture proof of a special binder, and there is the big operation effectiveness that it can manufacture cheaply. Since the translucency quantity dielectric constant inorganic dielectric is introduced in this invention as stated above, all the kinds that are not in the former of fluorescent substance offers the path which can be used effectively. Consequently, as well as full-color-izing which makes multiple color-ization of red, green, blue luminescence, etc. the start, since the EL element of white luminescence can also be manufactured cheaply and easily, an extensive application is expectable. An example explains this invention below.

[0009]

[Example 1] Translucency BaTiO<sub>3</sub> dielectric layer which distributed (Manganese Mn) addition zinc gallate (ZnGa<sub>2</sub>O<sub>4</sub>:Mn) fluorescent-substance powder:1 on ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO:3 using the sol-gel method as shown in drawing 1 : The deposition luminous layer which consists of 2 was formed. That is, the equimolar ratio mixture of barium ethoxide (Ba<sub>2</sub> (OEt)) and titanium isopropoxide (Ti<sub>4</sub> (O-i-Pr)) was first dissolved into the mixed solvent which consists of the methyl alcohol (CH<sub>3</sub>OH) and methoxy ethyl alcohol (CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>OH) of a volume ratio 3:2, and the sol was produced. Next, after mixing to homogeneity the ZnGa<sub>2</sub>O<sub>4</sub>:Mn fluorescent substance impalpable powder separately produced into this sol, the BaTiO<sub>3</sub> translucency gel which contains this fluorescent substance powder for this sol through hydrolysis and desiccation at 100 degrees C or less was formed, and it heat-treated at 500 degrees C succeedingly. a next spatter -- aluminum addition zinc-oxide (ZnO:aluminum) transparent electrode layer: -- aluminum counterelectrode layer:5 were formed for 4 on the surface of the opposite side, respectively, and the EL element was produced. The typical luminescence brightness-applied-voltage property of this EL element is shown in drawing 4 . High brightness green EL of highest luminescence brightness 1020 cd/m<sup>2</sup> was obtained from this drawing at the time of a 240V or 1kHz drive. Various fluorescent substances available instead of ZnGa<sub>2</sub>O<sub>4</sub>:Mn fluorescent substance powder, For example, it also sets to the EL element produced using Zn<sub>2</sub>SiO<sub>4</sub>:Mn, BO(Y, Gd)<sub>3</sub>:Eu, Y<sub>2</sub>O<sub>3</sub>:Eu, Y<sub>2</sub>O<sub>2</sub> S:Eu, BaMgAl<sub>10</sub>O<sub>17</sub>:Eu, or ZnS:Mn. Driver voltage and the luminescent color have realized 350V and green, 250V and red, 200V and red, 200V and red, and the engine performance that bears 250V and a blue list at use called 120V and yellow orange, respectively. Moreover, the particle size of the above-mentioned fluorescent substance powder was adjusted like drawing 2 , and even when the deposition luminous layer set to distributed part deposition or

fluorescent substance powder:1 made to all deposit from translucency BaTiO<sub>3</sub> ceramic-dielectric layer:2 in part was used, the almost same result was obtained. furthermore, the inside of about 1000 degrees C [ after settling Ga<sub>2</sub>O<sub>3</sub>:Mn fluorescent substance powder on ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO:3 like drawing 2 using the solution fully distributed in the acetone similarly ] air -- 5-hour heat treatment -- giving -- luminous layer:1 -- forming -- a it top -- this -- translucency BaTiO<sub>3</sub> dielectric-layer:2 were made to deposit In the EL element which formed and produced two electrodes like the account of Gokami, green luminescence of 940 cd/m<sup>2</sup> was obtained at the time of a 250V or 1kHz drive. Here, also when an EL element was produced similarly, using screen printing as the deposition method of application of this fluorescent substance, the almost same luminescence property as the case where it is based on a precipitation method was acquired.

[0010]

[Example 2] This fluorescent-substance powder that performs heat treatment for 20 minutes at 900 degrees C after precipitation spreading and among air on ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO:3 which show the Y<sub>2</sub>SiO<sub>5</sub>:Tb powder which is a green luminescence fluorescent substance to drawing 2 in the acetone solution containing it, and is shown in this drawing: 1 was made to fix on a ceramic sheet. The sol which hydrolyzed and produced the solution which consists the equimolar ratio mixture of the same approach as an example 1, i.e., barium ethoxide, (Ba<sub>2</sub> (OEt)), and titanium isopropoxide (Ti<sub>4</sub> (O-i-Pr)) of the methyl alcohol (CH<sub>3</sub>OH) and methoxy ethyl alcohol (CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>OH) of a volume ratio 3:2 after that was coated on this fluorescent substance with the dip method. Desiccation gelation was carried out in nitrogen-gas-atmosphere mind after that, heat treatment for 10 minutes was succeedingly performed at about 900 degrees C among air, and the deposition luminous layer containing Y<sub>2</sub>SiO<sub>5</sub>:Tb fluorescent substance powder:1 and translucency BaTiO<sub>3</sub> ceramic-dielectric layer:2 was formed. After repeating this actuation 15 times, aluminum counterelectrode layer:5 were formed for aluminum addition zinc-oxide (ZnO:aluminum) transparent electrode layer:4 on the surface of the opposite side by the spatter, respectively, and the EL element was produced. The typical luminescence brightness-applied-voltage property of this EL element was the same as that of drawing 4 almost. The highest luminescence brightness was 950 cd/m<sup>2</sup> at the time of a 220V or 1kHz drive. The luminescent color was green and high brightness was obtained. In addition, the dielectric layer which has translucency at the temperature of 400 degrees C or more in the case of the above-mentioned heat treatment: 2 was obtained. Moreover, also in the EL element which patternized the slurry which consists of this fluorescent substance powder on this ceramic sheet using screen printing, and carried out spreading formation, the almost same luminescence property was realizable. The highest luminescence brightness was green luminescence of 670 cd/m<sup>2</sup>. Moreover, Y<sub>2</sub>SiO<sub>5</sub>:Tb fluorescent substance powder : 1 is produced from the sol of an yttrium (Y) alkoxide and tetraethyl orthochromatic silicate (TEOS). It applies on this ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO:3 mentioned above using the spin coating method. After carrying out desiccation gelation, the almost same luminescence property was acquired also in the EL element which repeated the same process as 15 times, and formed and produced the deposition luminous layer which contains translucency BaTiO<sub>3</sub> ceramic-dielectric layer:2 with a sol-gel method still the more nearly same on it. In addition, the sol containing this fluorescent substance component was gelled on this ceramic sheet, the sol which contains this dielectric component succeedingly was introduced, and the almost same luminescence property was acquired also in the EL element which formed and produced this deposition luminous layer according to the heat treatment process for 60 minutes at 700 degrees C through humid gel and desiccation gel. Even if it used other various available fluorescent substances instead of Y<sub>2</sub>SiO<sub>5</sub>:Tb fluorescent substance powder, sufficient luminescence brightness which is equal to use similarly was obtained.

[0011]

[Example 3] it is shown in drawing 3 -- as -- as a base -- glass substrate: -- 6 tops -- ZnO:aluminum transparent electrode layer: -- 4 was formed and the deposition luminous layer containing translucency BaTiO<sub>3</sub> ceramic-dielectric layer:2 which distributed Ga<sub>2</sub>O<sub>3</sub>:Mn fluorescent substance powder:1 using the same production approach as this sol produced in the example 1 was formed on it. besides -- a vacuum deposition method -- aluminum counterelectrode layer: -- 5 was formed and the EL element was produced. Green EL of highest luminescence brightness 800 cd/m<sup>2</sup> was obtained at the time of the 250V or 1kHz drive of this EL element. Even if it used various available fluorescent substances instead of Ga<sub>2</sub>O<sub>3</sub>:Mn fluorescent substance powder, the almost same luminescence brightness was realizable. In addition, even if it used the alumina substrate as an opaque ceramic instead of the glass substrate, the same result was completely obtained.

[0012]

[Example 4] The same approach as an example 1 is used. As fluorescent substance powder Europium (Eu) addition yttrium oxide (Y<sub>2</sub>O<sub>3</sub>:Eu);a, Three kinds of Zn<sub>2</sub>(Si, germanium) O<sub>4</sub>:Mn;b and BaMgAl<sub>10</sub>O<sub>17</sub>:Eu;c are adopted. Screen printing is used. On ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO Width of face of 0.2mm, It applied carrying out patterning of the 10 sets, respectively having used stripe:A, :B, and :C with a die length [ of 50mm ], and a thickness of 0.01mm as 1 set, and the stripe pattern of the humid gel containing BaTiO<sub>3</sub> was produced. Then, desiccation gelation was carried out in nitrogen, heat treatment of 1 hour was succeedingly performed at about 500 degrees C among air, and the deposition luminous layer which consists of a, b, and c was formed. The mask was used on it, by the spatter, the aluminum addition zinc-oxide (ZnO:aluminum) transparent electrode layer was formed in the shape of a stripe, aluminum counterelectrode layer was formed in this deposition luminous layer part on the surface of the opposite side, respectively, and the EL element was produced. When this EL element was driven by 250V and 1kHz, the luminescence brightness of 800, 1000, and 120 cd/m<sup>2</sup> was respectively obtained from a, b, and c part in red, green, and blue. In addition, only each width of face of a, b, and c was set to 0.05mm, and when the EL element was produced and driven by the same approach as the above, luminescence which is visible to white \*\*\*\*\* yellowish green with the naked eye was presented. In addition, even if transposed to the glass substrate and the alumina substrate with the said ITO which coated the indium stannic acid ghost (ITO) transparence electric conduction film (transparent electrode) instead of, the almost same result was obtained. [ above-mentioned ferroelectric BaTiO<sub>3</sub> SERAMIKKUSHI-TO ] Moreover, it was effective to have inserted the black stripe which is not contributed to luminescence among Stripes A, B, and C, when raising contrast. Furthermore, 50 sets of try dot patterns which make 1 set a, b, and c of red with a diameter of 0.02mm, green, and blue luminescence instead of a stripe pattern were formed, when light was made to emit by the same drive as the above of the EL element which formed the transparent electrode layer for a passive-matrix drive, and the counterelectrode layer, respectively, and produced them, it is at the a, b, and c coincidence drive time and luminescence which looks being almost the same as that of a top to white \*\*\*\*\* yellowish green with the naked eye be presented.

[0013] This invention is not restricted to the above-mentioned example, and can use the fluorescent substance for Braun-tube CRT, the fluorescent substance for plasma displays, the fluorescent substance for the Hui-RUDOE missions display, the various fluorescent substances for lamps, the fluorescent substances for EL, and all fluorescent substance ingredients other than this for said fluorescent substance. Furthermore, using transparence electric conduction film, such as a tin oxide (SnO<sub>2</sub>) system, and an indium, a stannic acid ghost (ITO) system, in addition to the ZnO:aluminum transparent electrode layer illustrated in the above-mentioned example does not interfere at all. Moreover, the forming method can use a spatter, not only vacuum deposition but a sol-gel method, and all the other approaches. Here, BaTiO<sub>3</sub> was indicated as a translucency quantity dielectric constant inorganic dielectric layer as one example. However, this dielectric layer does not necessarily need to be BaTiO<sub>3</sub>.

[0014]

[Effect of the Invention] While according to this invention being unable to use as a luminous layer ingredient of an EL element conventionally and offering the path which can use the various fluorescent substances which were inadequate in property by the very easy and cheap approach, the high luminous efficiency which was not able to be attained in an old thin film fluorescent substance can be pulled out, and the effectiveness is greatest. Namely, since the oxygen acid salt system fluorescent substance, oxide system fluorescent substance, or sulfide system fluorescent substance known as the existing electron tube and the existing fluorescent substance for lamps is introduced, the high quality quantity crystallinity which fluorescent substance powder originally has can be used as it is, and it is effective in the ability to offer the EL element of high brightness luminescence in a easier process. And there is big effectiveness of not needing the special cure against moisture proof. Consequently, it is not caught by the class of old fluorescent substance, but white luminescence can also be easily realized as well as red, and green and blue multicolor luminescence and full color luminescence. Namely, power is greatly demonstrated as the full color luminescence plan type display, the multiple color or the white illumination lamp and the various pattern displays which harness the features which are field illuminants, or the high brightness white tooth-back light source for liquid crystal displays, and it is effective in the broad application which is not in the former being produced.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] -

[Drawing 3] : Cross-section structural drawing of the EL element by this invention

[Drawing 4] : The typical luminescence brightness-applied-voltage property Fig. from an EL element using ZnGa<sub>2</sub>O<sub>4</sub>:Mn as fluorescent substance powder

[Description of Notations]

- 1 .... Luminous layer which consists of fluorescent substance powder
- 2 .... Translucency quantity dielectric constant inorganic dielectric layer
- 3 .... Quantity dielectric constant dielectric ceramic sheet
- 4 .... Transparent electrode layer
- 5 .... Counterelectrode layer
- 6 .... Glass or ceramic sheet

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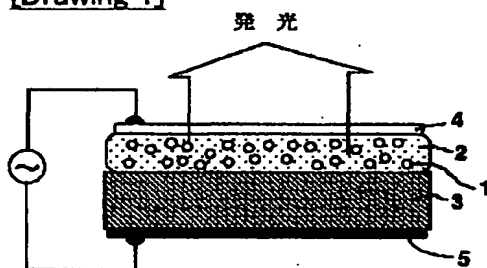
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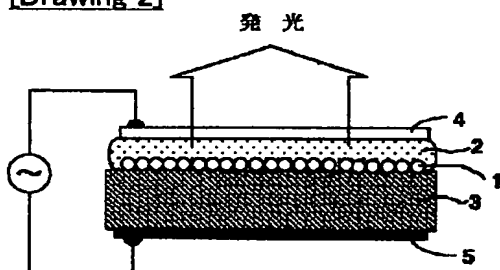
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## DRAWINGS

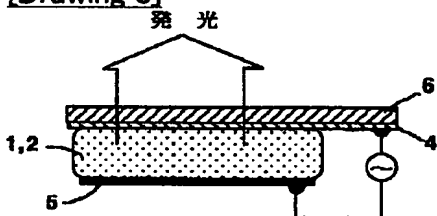
[Drawing 1]



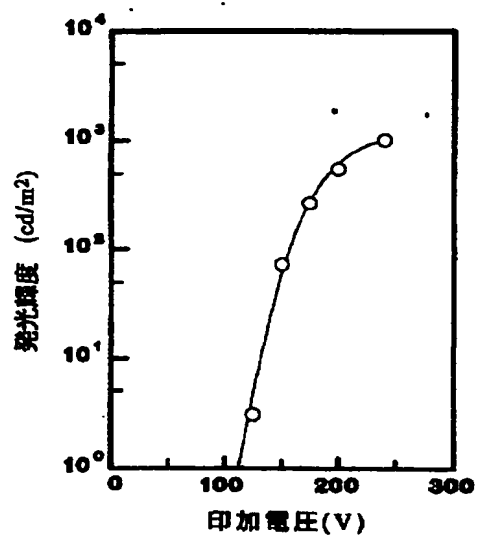
[Drawing 2]



[Drawing 3]



[Drawing 4]



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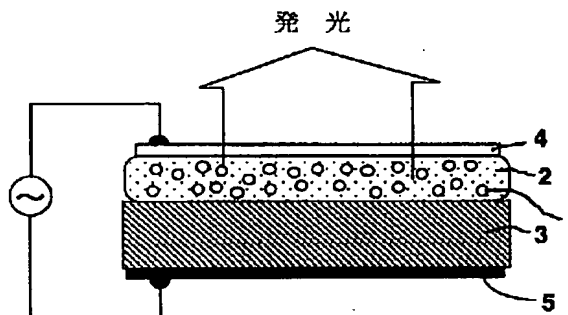
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(54) 【発明の名称】 エレクトロルミネッセンス素子及びその製造法

(57) 【要約】 (修正有)

【目的】 本発明では、従来利用されている硫化物系蛍光体粉末や酸化物系蛍光体粉末が持っている高品質高結晶性及びゾル・ゲル法等を用いて形成した低温で透光性と高誘電率を有する誘電体絶縁層を利用し、簡単な処理プロセスで高効率な発光を有するE L素子を実現する。

【構成】 本発明では、図1に示すように、基体3としてチタン酸バリウム等の強誘電体セラミックシート上、あるいはガラスまたはセラミック上に金属薄膜あるいは透明導電性薄膜を形成した電極層上に、少なくとも1種の蛍光体粉末1が図に示すごとく分散した透光性高誘電率誘電体層2からなる堆積発光層を形成し、透明電極層4と対向電極層5で挟んだ構造を有する該E L素子を提供する。また該堆積層が分散もしくは一部分散一部堆積あるいは全部堆積した蛍光体粉末1を含みかつ透光性を有する高誘電率誘電体層2から成っていることが重要である。



## 【特許請求の範囲】

【請求項1】 少なくとも1種の蛍光体粉末が分散もしくは一部分散一部基体上に堆積もしくは全部基体上に堆積した透光性高誘電率無機誘電体層からなる堆積発光層を基体上に形成し、透明電極層と対向電極層で挟んだ構造を特徴とするエレクトロルミネッセンス素子。

【請求項2】 前記基体が強誘電体セラミックシートである請求項1記載のエレクトロルミネッセンス素子。

【請求項3】 ガラスまたはセラミックである基体上に形成した金属薄膜あるいは透明導電性薄膜電極層上に請求項1記載の堆積発光層を形成しその上に透明導電性電極層あるいは金属電極層を形成してなることを特徴とする請求項1記載のエレクトロルミネッセンス素子。

【請求項4】 請求項1記載の堆積発光層を構成する透光性高誘電率無機誘電体層を基体上にゾル・ゲル法を用いて形成した後、制御雰囲気中にて該誘電体層の透光性を残す範囲の条件下で焼成もしくは熱処理を施して形成する堆積発光層を用いる請求項1、2または3記載のエレクトロルミネッセンス素子の製造法。

【請求項5】 バターニング技術を用いて2種以上の例えば赤、緑および青色で発光する3種の蛍光体からなるそれぞれの堆積発光層を請求項4記載の製造法を用いて同一面上に並べて形成する請求項4記載のエレクトロルミネッセンス素子の製造法。

【請求項6】 照光ランプ、表示装置を製造するのに使用される請求項4または5記載のエレクトロルミネッセンス素子の製造法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明はエレクトロルミネッセンス素子およびその製造法に関する。

## 【0002】

【従来の技術】エレクトロルミネッセンス素子（以下EL素子と呼ぶ）は、平面形固体発光表示装置への応用に対し古くから研究され、その実用化に対し根強い期待がある。このEL素子は、構造上、金属薄膜または透明導電性薄膜を形成したガラスまたはプラスチックフィルム基板上に結晶性の蛍光体発光層薄膜と誘電体絶縁層薄膜からなる片絶縁構造あるいは該蛍光体発光層薄膜を該誘電体絶縁層薄膜で挟んだ二重絶縁構造からなる薄膜上に透明電極層または金属薄膜電極層を形成したことを特徴とする薄膜形と蛍光体粉末を有機系誘電体バインダー中に均一に分散結着させてなる発光層を透明電極層と対向電極層で挟んだことを特徴とする有機分散形に分けられる。従来、EL素子の発光色に関しては、Mn添加硫化亜鉛（ZnS:Mn）系やテルビウム添加硫化亜鉛（ZnS:Tb）系二重絶縁構造交流駆動薄膜EL素子における黄橙色発光並びに緑色発光、そしてCu添加硫化亜鉛（ZnS:Cu）系有機分散形交流駆動薄膜EL素子における青緑色発光のもののみが実用されている。

## 【0003】

【発明が解決しようとする課題】上記した薄膜形EL素子の場合、片絶縁、二重絶縁構造のいずれのタイプでも蛍光体発光層と誘電体絶縁層が外部電源に対して直列に挿入され該発光層にかかる電界が著しく弱くなり高輝度発光が得られない。そのため透光性を有しかつ高誘電率の誘電体絶縁層の開発が課題となっている。一方該薄膜発光層の結晶性を高め、より高輝度発光を得るための高温熱処理がガラス基板を用いている場合には導入できないという問題がある。そこで低温で結晶性に優れた薄膜発光層を実現することが急務となっている。他方、該絶縁層として高誘電率セラミックシートを導入した薄膜EL素子が提案されているが、該絶縁層として機能させるための処理条件と該蛍光体発光層の処理条件が整合しないため処理プロセスが複雑なものになるという問題点がある。加えて蛍光体薄膜、特に最近の多元系酸化物蛍光体薄膜では、たとえ高温熱処理ができたとしてもその結晶性を向上させることは困難であるため蛍光体粉末のような高い発光効率を実現できないという問題がある。分散形EL素子の場合、薄膜EL素子に比べその素子構造が非常に簡単であるが、従来利用されているバインダーは誘電率が低く、そのため効率良く蛍光体に高電界を印加することが出来ないという問題があった。実用的に利用できる蛍光体は原理上Cu添加硫化亜鉛のみであり、その結果、高い発光輝度を有する素子が得られず、発光色も限られていた。しかも、硫化亜鉛等の硫化物系蛍光体材料は水分に敏感であるため、長時間素子を駆動させる場合には嚴重な防湿対策を施さなければならず高コスト化の最大の要因となっていた。

## 【0004】

【課題を解決するための手段】最近、発光層に水分に対し極めて強い酸化物系蛍光体を用いた高輝度EL素子の研究開発が活発化している。例えば、申請者らの発明になる特願平2-254649及び特願平2-256474、基板兼絶縁層として強誘電体である焼結チタン酸バリウム（BaTiO<sub>3</sub>）セラミック上にケイ酸塩系蛍光体のMn添加ケイ酸亜鉛（Zn<sub>2</sub>SiO<sub>4</sub>:Mn）なる薄膜発光層を形成したEL素子を実現している。ごく最近ではMn添加亜鉛ガレート（Zn<sub>2</sub>GaO<sub>4</sub>:Mn）〔特許申請中：特願平7-212332〕を用いた薄膜EL素子において、高輝度緑色発光を実現している。さらにMn添加酸化ガリウム-酸化カルシウム〔特許申請中：特願平9-95131〕を用いた薄膜EL素子において、高輝度発光を実現している。

【0005】本発明は、上記課題を一挙解決するため、従来から利用されている高結晶性硫化物系蛍光体粉末や上記したような高結晶性酸化物系蛍光体粉末とゾル・ゲル法により形成した低温で透光性と高誘電率を有する誘電体絶縁層を利用し、簡単な処理プロセスで高効率な多色発光を有するEL素子を実現しようとするものであ

る。即ち、本発明では、図1～図3に示しているように、基体として図1および図2のチタン酸バリウム等の強誘電体セラミックシート：3、あるいは図3の6で示すガラスまたはセラミック上に金属薄膜あるいは透明導電性薄膜：4を形成した電極層上に、少なくとも1種の蛍光体粉末が図1の1に示すごとく分散、もしくは図2の1に示すごとく一部分散一部堆積もしくは全部堆積した透光性高誘電率無機誘電体層：2からなる堆積発光層を形成し、透明電極層4と対向電極層5で挟んだ構造を有する該E L素子を提供する。ここで、該堆積発光層が蛍光体粉末を含みかつ透光性を有する高誘電率無機誘電体層から成っていることが重要である。申請者らは、従来、基体上に堆積させた粉末蛍光体とその上に該粉末蛍光体と同種もしくは異種薄膜蛍光体とからなる堆積層で構成される発光層を透明電極と対向電極とで挟んだ構造のE L素子を発明〔特許申請中：特願平8-95958〕している。このようなE L素子においては、基体上に堆積した粉末蛍光体に均一に高電界を印加することが必要となり、該素子に大きな電圧を加えなければならない。そのため絶縁層を導入して外部から非常に大きな電圧を印加するか、もしくは該絶縁層として高誘電率誘電体セラミックシート（不透明）を採用することにより該粉末蛍光体層に均一高電界を印加する手法がとられている。一方、本発明になるE L素子では、上に述べたような薄膜蛍光体層（透明な蛍光体堆積層を含む）に代わって従来実現できなかった透明な高誘電率無機誘電体層を導入したことにより、基体として強誘電体セラミックはもちろんのこと、ガラスやセラミックも利用でき、幅広い応用を可能としている点で、従来の薄膜E L素子の構成と大きく異なり画期的である。ところで、本発明になるE L素子を構成する該堆積発光層は、該蛍光体粉末と該誘電体層の各構成元素を含む金属塩、有機金属錯体、アルコキシド、アセテートあるいはアセチルアセトネート等の出発材料を用い、ゾルを作製し、例えば該ゾル中に蛍光体粉末を混合分散、もしくは一部分散一部堆積あるいは全部堆積させた後、または各々の構成元素を含む各ゾルを混合した後、該ゾルを加水分解、乾燥ゲルを形成し、引き続き透光性を残した範囲で熱処理を施すことにより本発明の目的を達成するものである。

【0006】尚、上記透明電極層は、公知の材料、例えば酸化錫系、酸化インジウム系、酸化亜鉛系またはII族、III族あるいはIV族元素を少なくとも1つ含む複合酸化物系透明導電膜材料を用い通常の真空蒸着法もしくはスパッタ法等により形成出来ることはもちろん、少なくとも1種のII族、III族あるいはIV族元素を含む金属塩、有機金属錯体、アルコキシド、アセテートあるいはアセチルアセトネートを含む有機溶液を用いた前記同様の工程を用いて形成することも出来る。

【0007】他方、本発明では上記した堆積発光層を形成した後、制御雰囲気中、即ち窒素ガス中もしくは空気

中あるいは酸素分圧を制御した酸化性雰囲気中において透光性を残した範囲で焼成もしくは熱処理を施すことにより該E L素子を製造出来ることを提案している。

【0008】

【作用】本発明に係るE L素子では、蛍光体粉末（一般に焼成粉である。）の持っている高品質高結晶性を最大限に活用できる構造を有している。また、球状蛍光体粉末の採用は充填率を高めるのに有効である。さらに蛍光体粉末は結晶性が優れているので、高電界印加時におけるホットエレクトロンの生成効率が高まることにより発光中心の励起効率も大幅に向上し、高い発光輝度が得られるという作用効果がある。さらに、本発明になるE L素子は単純な素子構造であることから実用的には非常に安価に製作できる。また本発明になる該素子構造は、該蛍光体粉末が基体上に一部分散一部堆積あるいは全部堆積している場合、金属-絶縁体-半導体という片絶縁構造あるいは金属-絶縁体-半導体-絶縁体という2重絶縁構造のE L素子を提供し、分散している場合、金属-絶縁体-半導体-絶縁体という2重絶縁構造のE L素子を提供できる自由度を有する。いずれの構造でも、該誘電体層が透光性を有するため該蛍光体からの光を有効に利用できることに加え、大きい誘電率を有しているの

で、該蛍光体に有効に高電界を印加できるという作用効果がある。さらには、本発明になるE L素子では該蛍光体が透光性高誘電率無機誘電体層で囲まれているため特別なバインダーの導入や防湿対策を施す必要もなく安価に製造できるという大きな作用効果がある。上に述べたように本発明では、透光性高誘電率無機誘電体を導入しているの

ので従来にないあらゆる種類の蛍光体が有効に利用できる道を提供するものである。その結果、赤、緑、青色発光等の多色化を初めとするフルカラー化は勿論、白色発光のE L素子も安価に、かつ容易に製造出来るようになるため広範な用途が期待出来る。以下に本発明を実施例により説明する。

【0009】

【実施例1】図1に示すように、ゾル・ゲル法を用いて強誘電体BaTiO<sub>3</sub>セラミックシート：3上にマンガ

ン(Mn)添加亜鉛ガレート(ZnGa<sub>2</sub>O<sub>4</sub>:Mn)蛍光体粉末：1を分散させた透光性BaTiO<sub>3</sub>誘電体層：2からなる堆積発光層を形成した。すなわち、まずバリウムエトキシド(Ba(OEt)<sub>2</sub>)とチタンイソプロポキシド(Ti(O-i-Pr)<sub>4</sub>)等の等モル比混合物を、容積比3：2のメチルアルコール(CH<sub>3</sub>OH)とメトキシエチルアルコール(CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>OH)からなる混合溶媒中に溶解しゾルを作製した。次に該ゾル中へ別途作製したZnGa<sub>2</sub>O<sub>4</sub>:Mn蛍光体微粉末を均一に混合した後、このゾルを加水分解、100℃以下での乾燥を経て該蛍光体粉末を含むBaTiO<sub>3</sub>透光性ゲルを形成し、引き続き500℃で熱処理を行なった。この後スパッタ法によりアルミニウム添加酸化亜鉛

(ZnO:Al)透明電極層:4を、反対側の表面にAl対向電極層:5をそれぞれ形成し、EL素子を作製した。このEL素子の典型的な発光輝度-印加電圧特性を図4に示す。同図より240V、1kHz駆動時において最高発光輝度1020cd/m<sup>2</sup>の高輝度緑色ELが得られた。ZnGa<sub>2</sub>O<sub>4</sub>:Mn蛍光体粉末の代わりに入手可能な各種蛍光体、例えばZn<sub>2</sub>SiO<sub>4</sub>:Mn、

(Y,Gd)BO<sub>3</sub>:Eu、Y<sub>2</sub>O<sub>3</sub>:Eu、Y<sub>2</sub>O<sub>3</sub>S:Eu、BaMgAl<sub>10</sub>O<sub>17</sub>:EuあるいはZnS:Mnを用いて作製したEL素子においても、駆動電圧・発光色はそれぞれ350V・緑色、250V・赤色、200V・赤色、200V・赤色、250V・青色並びに120V・黄橙色という使用に耐える性能を実現できた。また、図2のように上記蛍光体粉末の粒径を調節し、一部分散一部堆積もしくは全部堆積させた蛍光体粉末:1と透光性BaTiO<sub>3</sub>セラミック誘電体層:2からなる堆積発光層を用いた場合でもほぼ同様の結果が得られた。さらに、同じくGa<sub>2</sub>O<sub>3</sub>:Mn蛍光体粉末をアセトン中に十分に分散させた溶液を用い、図2のように強誘電体BaTiO<sub>3</sub>セラミックシート:3上に沈殿させた後、約1000℃の空气中で5時間熱処理を施し、発光層:1を形成し、その上に該透光性BaTiO<sub>3</sub>誘電体層:2を堆積させた。その後上記と同様に両電極を形成して作製したEL素子において、250V、1kHz駆動時940cd/m<sup>2</sup>の緑色発光が得られた。ここで、該蛍光体の堆積塗布方法としてスクリーン印刷法を用いて同様にEL素子を作製した場合も沈殿法による場合とほぼ同様の発光特性が得られた。

#### 【0010】

【実施例2】緑色発光蛍光体であるY<sub>2</sub>SiO<sub>5</sub>:Tb粉末を、それを含むアセトン溶液中にて図2に示す強誘電体BaTiO<sub>3</sub>セラミックシート:3上に沈殿塗布後、空气中900℃で20分間熱処理を施し同図に示す該蛍光体粉末:1をセラミックシート上に固定化させた。その後実施例1と同様の方法、即ちバリウムエトキシド(Ba(OEt)<sub>2</sub>)とチタンイソプロポキシド(Ti(O-i-Pr)<sub>4</sub>)の等モル比混合物を、容積比3:2のメチルアルコール(CH<sub>3</sub>OH)とメトキシエチルアルコール(CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>OH)からなる溶液を加水分解して作製したゾルをディップ法により該蛍光体上にコーティングした。その後窒素雰囲気中にて乾燥ゲル化し、引き続き空气中約900℃で10分間の熱処理を施し、Y<sub>2</sub>SiO<sub>5</sub>:Tb蛍光体粉末:1と透光性BaTiO<sub>3</sub>セラミック誘電体層:2を含む堆積発光層を形成した。この操作を15回繰り返した後、スパッタ法によりアルミニウム添加酸化亜鉛(ZnO:Al)透明電極層:4を、反対側の表面にAl対向電極層:5をそれぞれ形成し、EL素子を作製した。このEL素子の典型的な発光輝度-印加電圧特性は図4とほぼ同様であった。最高発光輝度は、220V、1kHz駆動時において9

50cd/m<sup>2</sup>であった。発光色は緑色で高輝度が得られた。尚、上記熱処理の際400℃以上の温度で透光性を有する誘電体層:2が得られた。また、該蛍光体粉末からなるスラリーをスクリーン印刷法を用いて該セラミックシート上にパターン化して塗布形成したEL素子においてもほぼ同様の発光特性を実現できた。その最高発光輝度は670cd/m<sup>2</sup>の緑色発光であった。また、Y<sub>2</sub>SiO<sub>5</sub>:Tb蛍光体粉末:1をイットリウム(Y)アルコキシドとテトラエチルオルソシリケート(TEOS)のゾルから作製し、スピンコーティング法を用いて上述した該強誘電体BaTiO<sub>3</sub>セラミックシート:3上に塗布、乾燥ゲル化した後、さらにその上に同じくゾル・ゲル法により透光性BaTiO<sub>3</sub>セラミック誘電体層:2を含む堆積発光層を15回同様の工程を繰り返し形成して作製したEL素子においてもほぼ同様の発光特性が得られた。尚、該蛍光体成分を含むゾルを該セラミックシート上でゲル化し、引き続き該誘電体成分を含むゾルを導入し、湿潤ゲル、乾燥ゲルを経て700℃で60分の熱処理工程で該堆積発光層を形成して作製したEL素子においてもほぼ同様の発光特性が得られた。Y<sub>2</sub>SiO<sub>5</sub>:Tb蛍光体粉末の代わりに他の入手可能な各種蛍光体を用いても同様に使用に耐える十分な発光輝度が得られた。

#### 【0011】

【実施例3】図3に示すように基体としてガラス基板:6上にZnO:Al透明電極層:4を形成し、その上に実施例1で作製した該ゾルと同様の作製方法を用いてGa<sub>2</sub>O<sub>3</sub>:Mn蛍光体粉末:1を分散させた透光性BaTiO<sub>3</sub>セラミック誘電体層:2を含む堆積発光層を形成した。この上に真空蒸着法によりAl対向電極層:5を形成し、EL素子を作製した。このEL素子の250V、1kHz駆動時において最高発光輝度800cd/m<sup>2</sup>の緑色ELが得られた。Ga<sub>2</sub>O<sub>3</sub>:Mn蛍光体粉末の代わりに入手可能な各種蛍光体を用いてもほぼ同様の発光輝度を実現できた。尚、ガラス基板の代わりに不透明セラミックとしてアルミナ基板を使用しても全く同様の結果が得られた。

#### 【0012】

【実施例4】実施例1と同じ方法を用い、蛍光体粉末としてユーロピウム(Eu)添加酸化イットリウム(Y<sub>2</sub>O<sub>3</sub>:Eu):a、Zn<sub>2</sub>(Si,Ge)O<sub>4</sub>:Mn:b、およびBaMgAl<sub>10</sub>O<sub>17</sub>:Eu:cの3種類を採用し、スクリーン印刷法を用いて強誘電体BaTiO<sub>3</sub>セラミックシート上に幅0.2mm、長さ50mm、厚さ0.01mmのストライプ:A、:B、:Cを1組としてそれぞれ10組をパターンニングしながら塗布し、BaTiO<sub>3</sub>を含む湿潤ゲルのストライプパターンを作製した。その後、窒素中にて乾燥ゲル化し、引き続き空气中約500℃で1時間の熱処理を施し、a、b、cから構成される堆積発光層を形成した。その上にマスクを用

いて該堆積発光層部分にスパッタ法によりストライプ状にアルミニウム添加酸化亜鉛 ( $\text{ZnO}:\text{Al}$ ) 透明電極層を、反対側の表面に  $\text{Al}$  対向電極層をそれぞれ形成し、EL素子を作製した。このEL素子を250V、1kHzで駆動したところ、a、b、c部分からそれぞれ赤、緑、青色で各々800、1000、120cd/m<sup>2</sup>の発光輝度を得られた。尚、a、b、cの幅のみをいずれも0.05mmとして上記と同様の方法でEL素子を作製し駆動したところ肉眼では白っぽい黄緑色に見える発光を呈した。尚、上記強誘電体  $\text{BaTiO}_3$ 、セラミックシート

10 の代わりにインジウム錫酸化物 ( $\text{ITO}$ ) 透明導電膜 (透明電極) をコーティングしたガラス基板や同  $\text{ITO}$  付きアルミナ基板に置き換えてもほぼ同様の結果が得られた。また、ストライプA、B、Cの間に発光に寄与しないブラックストライプを挿入することはコントラストを向上させる上で効果的であった。さらに、ストライプパターン

20 の代わりに直径0.02mmの赤、緑、青発光のa、b、cを1組とするトライドットパターンを50組形成し、単純マトリクス駆動用透明電極層と対向電極層をそれぞれ形成して作製したEL素子を上記同様の駆動により発光させたところ、a、b、c同時駆動時で、上とはほぼ同様に肉眼では白っぽい黄緑色に見える発光を呈した。

【0013】本発明は上記実施例に限られるものではなく、前記蛍光体には、ブラウン管CRT用蛍光体、プラズマディスプレイ用蛍光体、フィールドエミッションディスプレイ用蛍光体、各種ランプ用蛍光体、EL用蛍光体そしてこれ以外の蛍光体材料の全てが利用できる。さらに、上記実施例で例示した  $\text{ZnO}:\text{Al}$  透明電極層以外に酸化錫 ( $\text{SnO}_2$ ) 系やインジウム・錫酸化物 ( $\text{ITO}$ ) 系等の透明導電膜を使用することは一向に差し支えない。また、その形成法はスパッタ法や蒸着法に限らずソル・ゲル法やその他のあらゆる方法が利用できる。ここでは1例として透光性高誘電率無機誘電体層と\*

\*して  $\text{BaTiO}_3$  を開示した。しかし、該誘電体層は、必ずしも  $\text{BaTiO}_3$  である必要はない。

【0014】

【発明の効果】本発明によれば、従来、EL素子の発光層材料として利用出来なかったり、また特性的に不十分であった各種蛍光体を極めて簡単に安価な方法で利用出来る道を提供するとともに、これまでの薄膜蛍光体では達成できなかった高い発光効率を引き出すことが出来、その効果は絶大である。即ち既存の電子管やランプ用蛍光体として知られている酸素酸塩系蛍光体や酸化物系蛍光体あるいは硫化物系蛍光体を導入しているので蛍光体粉末が本来持っている高品質高結晶性をそのまま利用でき、より簡単なプロセスで高輝度発光のEL素子を提供できるという効果がある。しかも特別な防湿対策を必要としないという大きな効果がある。その結果、これまでの蛍光体の種類にとらわれず赤、緑、青色の多色発光やフルカラー発光は勿論、白色発光をも容易に実現することが出来る。即ち面発光体である特長を活かすフルカラー発光平面形ディスプレイ、多色もしくは白色照光ランプや各種パターン表示もしくは液晶表示装置用高輝度白色背面光源として大いに威力を発揮し、従来にない幅広い用途が生み出されるという効果がある。

【図面の簡単な説明】

【図1】～

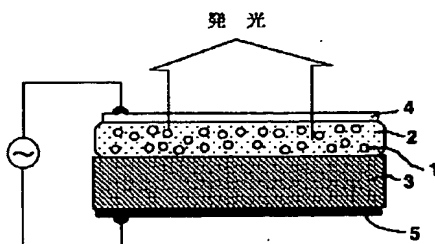
【図3】：本発明によるEL素子の断面構造図

【図4】：蛍光体粉末として  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  を用いたEL素子からの典型的な発光輝度-印加電圧特性図

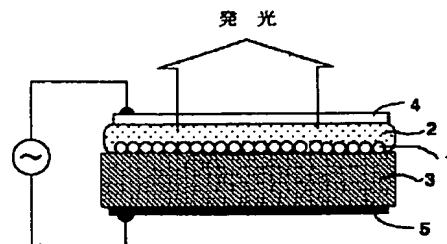
【符号の説明】

- 1・・・蛍光体粉末からなる発光層
- 2・・・透光性高誘電率無機誘電体層
- 3・・・高誘電率誘電体セラミックシート
- 4・・・透明電極層
- 5・・・対向電極層
- 6・・・ガラスまたはセラミックシート

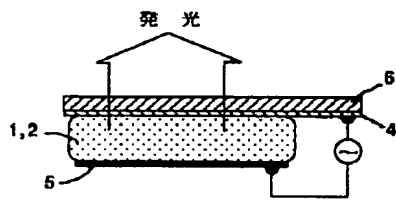
【図1】



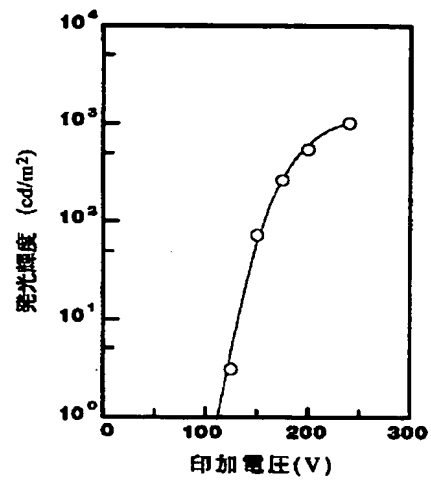
【図2】



【図3】



【図4】



フロントページの続き

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